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(58) Field of search

B5B

B5N

Selected US specifications from IPC sub-class B29D

(54) **Manufacturing method of laminate film**

(57) A high strength laminate sheet which comprises a film of a polymer adapted to form an anisotropic melt phase (liquid crystal) and a film of a thermoplastic polymer is produced by laminating the films, including moulding each film at the same time.

SPECIFICATION

Manufacturing method of laminate film

5 The present invention relates to an industrially advantageous manufacturing method for continuously manufacturing a high strength multi-layer film containing, as at least one layer, a polymer adapted to form anisotropic melt-phase. 5

Polymers known as thermotropic liquid crystal polymers and which are adapted to give anisotropic melt phase are known to have very high strength in their oriented direction because of the anisotropy of their orientation, but their strength in the perpendicular direction to their oriented direction is notably lower, as compared with that in the oriented direction, so that either it is difficult to form it into film by usual continuous process or the film's utility is limited in many uses. 10

Heretofore, proposed are manufacturing methods of sheets or films formed of thermotropic liquid crystal polymers which show desirable characteristics in many fields. For example, Laid-Open Patent No. 4626/1981, Laid-Open Patent No. 46727/1981 and Laid-Open Patent No. 161821/1980 propose internal plasticization of molecular structure and plasticization by blending the polymers with plasticizers, etc., but these sheets or films are rather melt-processing with their anisotropy extremely reduced; as a consequence, their strength is sacrificed. 15

Laid Open Patent No. 31718/1983 proposes a multiaxially oriented laminate formed by laminating uniaxial sheets of thermotropic liquid crystal polymers, in which high strength is achieved by laminating in multi-layers sheets oriented in different axial directions. But it is difficult to laminate 2 sheets in a continuous process in such a way that their axial lines make definite angles to each other. This method is not economical and is not satisfactory as an industrial manufacturing method. 20

The present invention has as its object resolving the technical theme of film-forming with such polymers, while maintaining high orientation and high strength, characteristics which the thermotropic liquid phase polymers possess. 25

Thus the present invention provides a method for continuously manufacturing a high strength laminate film on industrial scale and relates to a manufacturing method of laminate film characterized in that in manufacturing a multi-layer sheet and/or a multi-layer film formed of a polymer adapted to form anisotropic melt phase and a thermoplastic polymer having film forming ability, at least one of the polymers above-mentioned is laminated by way of fusion molding. 30

In the invention as defined in other words, a laminate sheet which comprises a film of a polymer adapted to form the anisotropic melt phase and a film of a thermoplastic polymer having the film-forming property is produced by laminating at least one of both polymers. One of both polymers is first moulded to film and the other polymer is laminated thereon. Alternatively both polymers may be moulded to film at the same time and laminated on each other. 35

According to this invention, a method capable of industrial continuous production of multi-layer laminate film in which the strength in the direction of orientation is mostly dependent on the first polymer adapted to show anisotropic melt phase, while the strength in the lateral axial direction is mostly dependent on the thermoplastic polymer having film-forming ability, or the second polymer, and the film forming ability is conferred on the second thermoplastic polymer. 40

The polymers adapted to give anisotropic melt phase which is used for laminate film of this invention means polymer compositions which show optical anisotropy, when melted, and which are thermoplastic and melt-processing. They are generally classified as thermotropic liquid crystal polymers.

45 Polymers adapted to form such anisotropic melt phase have a property that in their fused state, polymer molecule chains show regular parallel arrangement. The state in which molecules are arranged in this fashion is often called liquid crystal state or nematic phase of liquid crystalline material. Such polymers are generally slender, flat and fairly high in rigidity along longer axis of molecule and are normally manufactured from monomers having a plurality of chain extended bonds being either in coaxial or parallel relation to each other. 50

The property of the anisotropic melt phase may be checked for sure by the commonly used method of polarization inspection based on utilization of orthogonal polarizers. More particularly, the confirmation of the anisotropic melt phase may be made by observing a sample put on a Leitz hot stage at a multiplicity of 40 in nitrogen atmosphere, using a Leitz polarization microscope. The aforementioned polymers are optically anisotropic. Thus they permit light to pass through, when checked between orthogonal polarizers. If a sample is optically anisotropic, a polarized light will pass through it, even if it is in stationary state. 55

Mentioned as the components of the polymers adapted to form anisotropic fused phase such as the aforementioned are:

- ① Those comprising one or more of aromatic dicarboxylic acids and acyclic dicarboxylic acids;
- 60 ② Those comprising one or more of aromatic diols, acyclic diols and aliphatic diols;
- ③ Those comprising one or more of aromatic hydroxycarboxylic acids;
- ④ Those comprising one or more of aromatic thiol carboxylic acids;
- ⑤ Those comprising one or more of aromatic dithiols and aromatic thiol phenols; and
- ⑥ Those comprising one or more of aromatic hydroxyamines and aromatic diamines;

65 and the polymers adapted to form anisotropic fused phase are composed of the following combinations: 65

- I) Polyesters formed of ① and ② ;
 II) Polyesters formed of ③ only ;
 III) Polyesters formed of ① , ② and ③ ;
 IV) Polythiol esters formed of ④ only ;
 V) Polythiol esters formed of ① and ⑤ ;
 VI) Polythiol esters formed of ① , ④ and ⑤ ;
 VII) Polyester amides formed of ① , ③ and ⑥ ; and
 VIII) Polyester amides formed of ① , ② , ③ and ⑥ .
- Although not included in the categories of combinations of components above-mentioned, aromatic polyazomethines are included as polymers adapted to form anisotropic fused phase. Mentioned as particular examples of such polymers are: Poly (nitrilo-2-methyl-1,4-phenylene-nitriloethylidene-1,4-phenylene ethylidene), poly (nitrilo-2-methyl-1,4-phenylene nitriloethylidene-1,4-phenylene methylidene) and poly (nitrilo-2-chloro-1,4-phenylene nitrilomethylidene-1,4-phenylene methylidene).
- Further, although not included in the categories of the combinations of the aforementioned components, polyester carbonates are included as the polymers adapted to form anisotropic fused phase. Some of them essentially comprise 4-oxybenzoyl units, dioxyphenyl units, dioxycarbonyl units and terephthaloyl units.
- In the following, such compounds which are usable as components of I) – VIII) above-mentioned are listed hereunder:
- Mentioned as aromatic dicarboxylic acids are: Aromatic dicarboxylic acids such as terephthalic acid, 4,4'-diphenyl dicarboxylic acid, 4,4'-triphenyl dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, diphenyl ether-4,4'-dicarboxylic acid, diphenoxyethane-4,4'-dicarboxylic acid, diphenoxybutane-4,4'-dicarboxylic acid, diphenylethane-4,4'-dicarboxylic acid, isophthalic acid, diphenyl ether-3,3'-dicarboxylic acid, diphenoxyethane-3,3'-dicarboxylic acid, diphenyl ethane-3,3'-dicarboxylic acid and naphthalene-1,6-dicarboxylic acid or alkyl, alkoxy or halogen substitutes of the aforementioned aromatic dicarboxylic acids such as chloroterephthalic acid, dichloroterephthalic acid, bromoterephthalic acid, methyl terephthalic acid, dimethyl terephthalic acid, ethyl terephthalic acid, methoxyterephthalic acid and ethoxyterephthalic acid.
- Mentioned as the acyclic dicarboxylic acids are: Acyclic dicarboxylic acids such as trans-1,4-cyclohexane dicarboxylic acid, cis-1,4-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid, etc., or alkyl, alkoxy or halogen substitutes of the aforementioned acyclic dicarboxylic acids such as trans-1,4-(1-methyl)-cyclohexane-dicarboxylic acid, trans-1,4-(1-chloro)-cyclohexane dicarboxylic acid, etc.
- Mentioned as aromatic diols are: Aromatic diols such as hydroquinone, resorcinol, 4,4'-dihydroxydiphenyl, 4,4'-dihydroxytriphenyl, 2,6-naphthalenediol, 4,4'-dihydroxydiphenyl ether, bis (4-hydroxyphenoxy)-ethane, 3,3'-dihydroxydiphenyl, 3,3'-dihydroxydiphenyl ether, 1,6-naphthalenediol, 2,2-bis(4-hydroxyphenyl) propane, 2,2-bis (4-hydroxyphenyl) methane, etc., or alkyl, alkoxy or halogen substitutes of the aforementioned aromatic diols such as chlorohydroquinone, methyl hydroquinone, 1-butyl hydroquinone, phenyl hydroquinone, methoxyhydroquinone, phenoxyhydroquinone, 4-chlororesorcinol, 4-methyl resorcinol, etc.
- Mentioned as the acyclic diols are: Acyclic diols such as trans-1,4-cyclohexanediol, cis-1,4-cyclohexanediol, trans-1,4-cyclohexane dimethanol, cis-1,4-cyclohexane dimethanol, trans-1,3-cyclohexanediol, cis-1,2-cyclohexanediol and trans-1,3-cyclohexanedimethanol or alkyl, alkoxy or halogen substitutes of the aforementioned acyclic diols such as trans-1,4- (1-methyl) cyclohexanediol and trans-1,4-(1-chloro) cyclohexanediol.
- Mentioned as the aliphatic diols are: Straight chain or branched aliphatic diols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, neopentyl glycol, etc.
- Mentioned as the aromatic hydroxycarboxylic acids are: Aromatic hydroxycarboxylic acids such as 4-hydroxybenzoic acid, 3-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid, 6-hydroxy-1-naphthoic acid, etc., or alkyl, alkoxy or halogen substitutes of aromatic hydroxycarboxylic acids such as 3-methyl-4-hydroxybenzoic acid, 3,5-dimethyl-4-hydroxybenzoic acid, 2,6-dimethyl-4-hydroxybenzoic acid, 3-methoxy-4-hydroxybenzoic acid, 3,5-dimethoxy-4-hydroxybenzoic acid, 6-hydroxy-5-methyl-2-naphthoic acid, 6-hydroxy-5-methoxy-2-naphthoic acid, 3-chloro-4-hydroxybenzoic acid, 2-chloro-4-hydroxybenzoic acid, 2,3-dichloro-4-hydroxybenzoic acid, 3-5-dichloro-4-hydroxybenzoic acid, 2,5-dichloro-4-hydroxybenzoic acid, 3-bromo-4-hydroxybenzoic acid, 6-hydroxy-5-chloro-2-naphthoic acid, 6-hydroxy-7-chloro-2-naphthoic acid, 6-hydroxy-5,7-dichloro-2-naphthoic acid, etc.
- Mentioned as the aromatic mercaptocarboxylic acid are: 4-Mercaptobenzoic acid, 3-mercaptobenzoic acid, 6-mercapto-2-naphthoic acid, 7-mercapto-2-naphthoic acid, etc.
- Mentioned as the aromatic dithiols are: Benzene-1, 4-dithiol, benzene-1,3-dithiol, 2,6-naphthalene dithiol and 2,7-naphthalene dithiols, etc.
- Mentioned as the aromatic mercaptophenols are: 4-Mercaptophenol, 3-mercaptophenol, 6-mercaptophenol and 7-mercaptophenol, etc.
- Mentioned as aromatic hydroxyamines and aromatic diamines are: 4-Aminophenol, N-methyl-4-aminophenol, 1,4-phenylenediamine, N-methyl-1,4-phenylenediamine, N, N'-dimethyl-1,4-phenylenediamine, 3-aminophenol, 3-methyl-4-aminophenol, 2-chloro-4-aminophenol, 4-amino-1-naphthol, 4-amino-4'-hydroxydiphenyl, 4-amino-4'-hydroxydiphenyl ether, 4-amino-4'-hydroxydiphenyl methane, 4-amino-4'-hydroxydiphenyl sulfide, 4,4'-diaminophenyl sulfide (thiodianiline), 4,4'-diaminophenyl-sulfone, 2,5-diaminotoluene, 4,4'-ethylene dianiline, 4,4'-diaminodiphenoxyethane, 4,4'-diaminodiphenyl methane

(methylene dianiline), 4,4'-diaminodiphenyl ether (oxydianiline), etc.

Of the aforementioned polymers I)–VIII) composed of the aforementioned components, there exist those which are adapted to form anisotropic melt phase and those which are not, depending on their components, their composition ratios and sequence distributions in these polymers. The polymers used in accordance with this invention are restricted to those of the aforementioned polymers adapted to form anisotropic melt phase.

The polyesters of the aforementioned I), II) and III) and polyester amides of VIII), being polymers adapted to form anisotropic fused phase which are desirable for use in exercising this invention, may be produced by various ester forming methods which enable mutual reactions of organic monomer compounds having functional groups which play the role of forming the required repetitive units by condensation. For example, such functional groups of these organic monomer compounds may include carboxyl, hydroxyl, ester and acyloxy groups, acid halides and amine group. The aforementioned organic monomer compounds may be reacted with each other by fusion acidolytic process, while keeping any heat exchange fluid out of existence. According to this method, first, fused solution of the reaction materials is formed by heating the monomers together. As the reactions are continued, solid polymer particles become being suspended in the liquid. For the purpose of facilitating removal of volatile matters (e.g., acetic acid or water) which are produced as byproducts at the final stage of condensation, the system may be put under vacuum.

The slurry polymerization process may be employed for forming perfect aromatic polyesters which are preferred for use in exercising this invention. By this method, the solid product is obtained in the state of being suspended in a heat exchanging medium.

Whichever process, the aforementioned fusion acidolytic process or the slurry polymerization process, is employed, the organic monomer reaction materials which are to derive the perfect aromatic polyesters may be put to use for the reactions in their denatured form (thus, as lower acyl esters) in which the hydroxyl groups of such monomers at normal temperature are esterified. As lower acyl groups, those with carbon atoms approx. 2–4 in number are preferable. Preferably, acetic acid esters of such organic monomer reaction materials are put to use for the reactions.

Further mentioned as typical examples of catalyzers which are arbitrarily usable either in the fusion acidolytic process or slurry process are: Gaseous acid catalyzers, etc., such as dialkyl tin oxide (e.g., dibutyl tin oxide), diallyl tin oxide, titanium dioxide, antimony trioxide, alkoxytitanium silicate, titanium alkoxide, alkali and alkaline earth metal salts of carboxylic acids (e.g., zinc acetate), Lewis acids (e.g., BF_3), hydrogen halides (e.g., HCl), etc. The amounts of catalyzers used generally should be approx. 0.001–1% by weight, particularly, approx. 0.01–0.2% by weight, based on the total weight of monomers.

The perfect aromatic polymers suitable for use in exercising this invention show a tendency of being substantially insoluble in common solvents and therefore, they are not suitable for forming from solution. However, as already described, these polymers permit easy forming by the ordinary fusion forming process. Particularly desirable perfect aromatic polymers are soluble in some degree in pentafluorophenol.

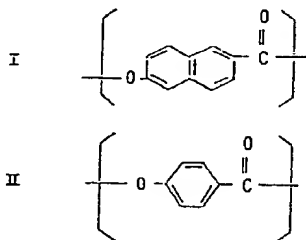
The perfect aromatic polyesters preferable for use in exercising this invention generally should have weight average molecular weights of approx. 2,000–200,000, preferably, approx. 10,000–50,000 and more preferably, approx. 20,000–25,000. On the other hand the preferable perfect aromatic poly (ester-amides) generally should have molecular weights of approx. 5,000–50,000, preferably, approx. 10,000–30,000, e.g., 15,000–17,000. Measurement of such molecular weights may be made by gel permeation chromatography and other standard measuring methods which do not accompany solution forming of polymer, for example, by determining terminal groups by infrared spectroscopy on compression molded films. Or the measurement of molecular weight may be made by light scattering methods on the solution of polymer in pentafluorophenol.

The aforementioned perfect aromatic polyesters and polyester amides, when dissolved in pentafluorophenol at 60°C at a concentration of 0.1 weight %, generally give logarithmic viscosity (I.V.) of at least approx. 2.0 dl/g, for example, approx. 2.0–10.0 dl/g.

The polyesters adapted to form anisotropic fused phase which are particularly desirable for use in exercising this invention should contain more than approx. 10 mol % of naphthalene part containing repetitive units such as 6-hydroxy-2-naphthoyl, 2,6-dioxynaphthalene and 2,6-dicarboxynaphthalene, etc. Desirable polyester amides should contain repetitive units of the aforementioned naphthalene part and another part comprising 4-aminophenol or 1,4-phenylene diamine.

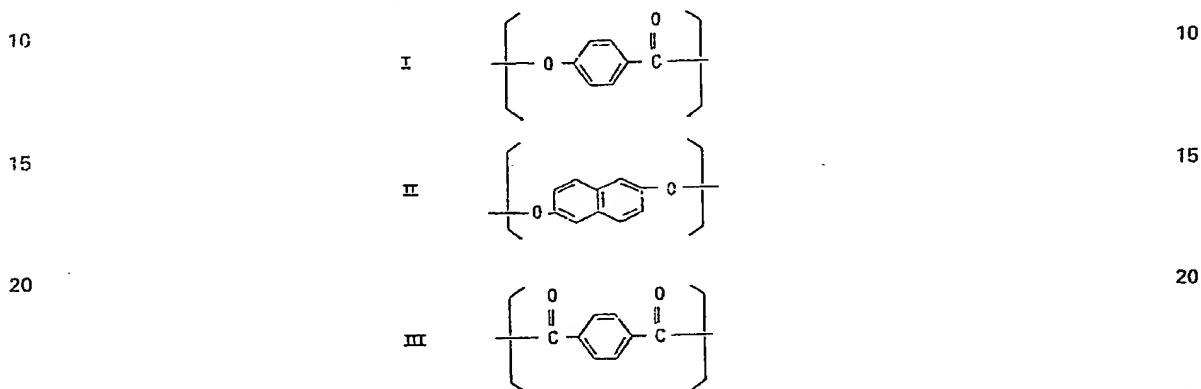
Particular examples are given hereunder:

(1) Polyesters essentially composed of the following repetitive units I and II.



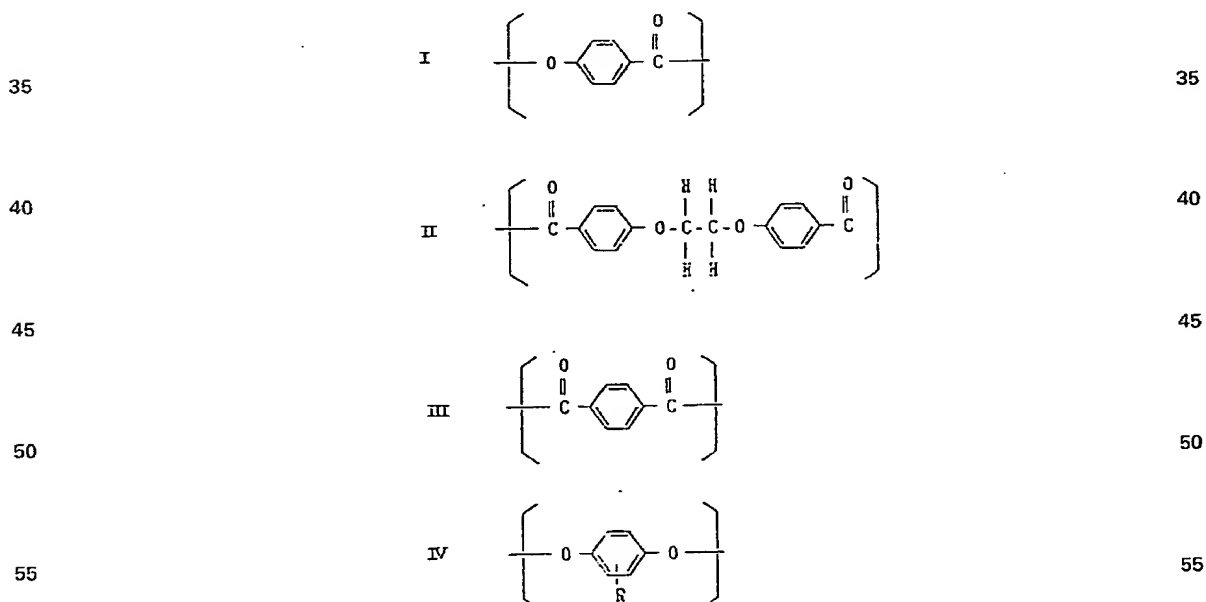
The polyesters contain approx. 10–90 mol % of unit I and approx. 10–90 mol % of unit II. In one mode, the units I exist up to approx. 65–85 mol %, preferably, approx. 70–80 mol % (e.g., about 75 mol %). In another mode, the units II exist at as far lower concentrations as approx. 15–35 mol %, preferably, approx. 20–30 mol %, and at least part of hydrogen atoms bonded to the ring(s) are allowed to be substituted, as the case may be, by any substituent radicals selected from among a group consisting of alkyl groups with number of carbon atoms 1–4, alkoxyl groups with number of carbon atoms 1–4, halogens, phenyls, substituted phenyls and their combinations.

(2) Polyesters essentially composed of the following repetitive units I, II and III:



These polyesters contain approx. 30–70 mol % of unit I. They should preferably, contain approx. 40–60 mol % of unit I, approx. 20–30 mol % of units II and approx. 20–30 mol % of unit III and at least part of hydrogen atoms bonded to the ring(s) are allowed to be substituted, as the case may be, by any substituent radicals selected from among a group consisting of alkyl groups with the number of carbons 1–4, alkoxyl groups with the number of carbons 1–4, halogens, phenyls, substituted phenyls and their combinations.

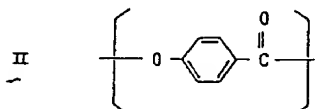
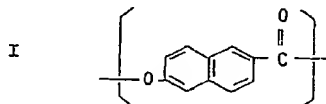
(3) Polyesters essentially composed of the following repetitive units I, II, III and IV:



(where R means methyl, chloro, bromo or their combinations, being substituent radicals to hydrogen atoms on benzene ring(s).) They contain approx. 20–60 mol % of unit I, approx. 5–18 mol % of unit II, approx. 5–35 mol % of unit III and approx. 20–40 mol % of unit IV. These polyesters should preferably contain approx. 35–45 mol % of unit I, approx. 10–15 mol % of unit II, approx. 15–25 mol % of unit III and approx. 25–35 mol % of unit IV. Provided that sum total mol concentration of units II and III is substantially equal to the mol concentration of units IV. At least part of the hydrogen atoms which are bonded to the ring(s) are allowed to be substituted, as the case may be, by any substituent radical(s) selected from among a group consisting of alkyl radicals with the number of carbon atoms 1–4, alkoxyl radicals with the number of carbon atoms 1–4,

halogens, phenyls, substituted phenyls and their combinations. These perfect aromatic polyesters, when dissolved at 60°C in pentafluorophenol at a concentration of 0.3 W/V %, generally give their logarithmic viscosities at least 2.0 dl/g, e.g., 2.0–10.0 dl/g.

(4) Polyesters essentially composed of the following repetitive units I, II, III and IV:

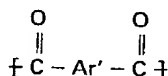


III Dioxyallyl unit represented by a general formula:



(where Ar means a divalent group having at least one benzene ring.)

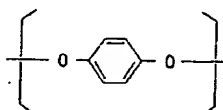
IV Dicarboxyallyl unit represented by a general formula:



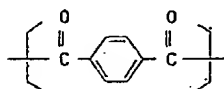
(where Ar' means a divalent group having at least one benzene ring). They contain approx. 20–40 mol % of unit I, more than 10 mol % but less than approx. 50 mol % of unit II, more than 5 mol % but less than approx. 30 mol % of unit III and more than 5 mol % but less than approx. 30 mol % of unit IV. These polyesters should preferably contain approx. 20–30 mol % (e.g., approx. 25 mol %) of unit I, approx. 25–40 mol % (e.g., approx. 35 mol %) of unit II, approx. 15–25 mol % (e.g., approx. 20 mol %) of unit III and approx. 15–25 mol % (e.g., approx. 20 mol %) of unit IV. And at least part of hydrogen atoms bonded to the ring(s) are allowed to be substituted by any substituent radicals selected from among a group consisting of alkyl radicals with the number of carbon atoms 1–4, alkoxy radicals with the number of carbon atoms 1–4, halogens, phenyls, substituted phenyls and their combinations.

The units III and IV should preferably be symmetric in the sense that the divalent bonds which are joining each one of them to other units on both sides thereof inside the polymer main chain are symmetrically arranged on 1 or 2 or more of benzene rings (for example, when they exist on a naphthalene ring, they are arranged mutually at para positions or at diagonal ring positions). However, non-symmetrical units which may be derived from resorcinol and isophthalic acid are also usable.

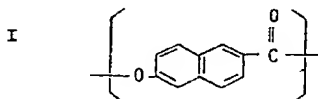
Desirable dioxyallyl unit III is:



desirable dicarboxyallyl unit is:



(5) Polyesters essentially composed of the following repetitive units I, II, and III:

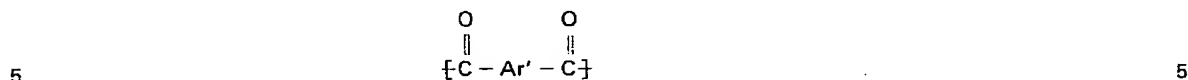


II Dioxyallyl unit represented by a general formula



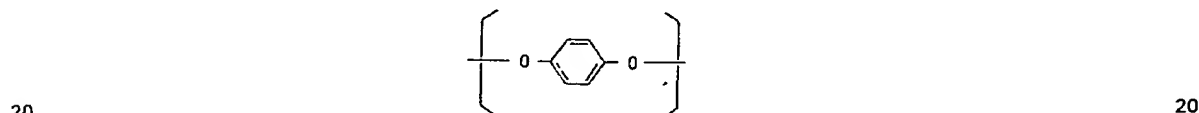
(where Ar means a divalent radical having at least one benzene ring)

III Dicarboxyallyl unit represented by a general formula

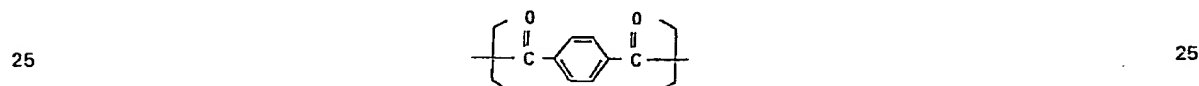


(where Ar' means a divalent radical containing at least one benzene ring). They contain approx. 10–90 mol % of unit I, 5–45 mol % of unit II and 5–45 mol % of unit III. These polyesters should preferably contain approx. 20–80 mol % of unit I, approx. 10–40 mol % of the unit II and approx. 10–40 mol % of the unit III. More preferably, they should contain approx. 60–80 mol % of unit I, approx. 10–20 mol % of unit II and approx. 10–20 mol % of unit III. And at least part of hydrogen atoms bonded to the ring(s) are allowed to be substituted, as the case may be, by any substituent radical(s) selected from among a group consisting of alkyl radicals with the number of carbon atoms 1–4, alkoxyl radicals with the number of carbon atoms 1–4, halogens, phenyls, substituted phenyls and their combinations.

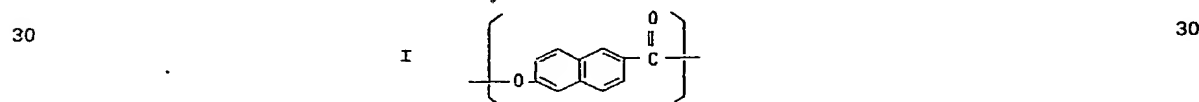
Desirable dioxyallyl unit II should be:



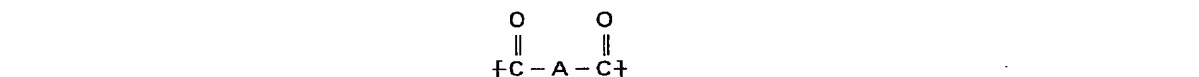
and desirable dicarboxyallyl unit III should be:



(6) Polyester amides essentially composed of the following repetitive units I, II, III and IV:



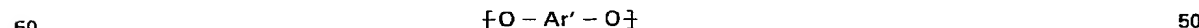
II A general formula



(where A means a divalent radical having at least one benzene ring or divalent trans-cyclohexane radical)
III A general formula

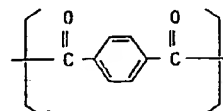


(where Ar means a divalent radical having at least one benzene ring; Y represents O, NH or NR; and Z stands for NH or NR; where R means alkyl radicals or allyl radicals with the number of carbon atoms 1–6)
IV A general formula

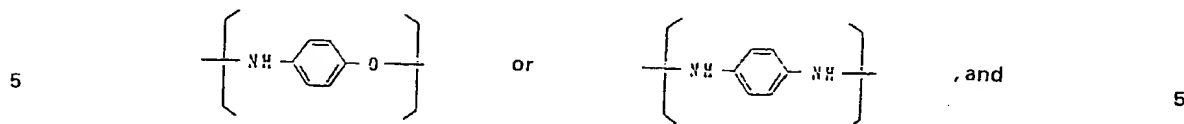


(where Ar' means a divalent radical having at least one benzene ring). They contain approx. 10–90 mol % of unit I, approx. 5–45 mol % of unit II, approx. 5–45 mol % of unit III and approx. 0–40 mol % of unit IV. And at least part of hydrogen atoms bonded to the ring(s) are allowed to be substituted, as the case may be, by any substituent radicals selected from among a group consisting of alkyl radicals with the number of carbon atoms 1–4, alkoxyl radicals with the number of carbon atoms 1–4, halogens, phenyls, substituted phenyls and their combinations.

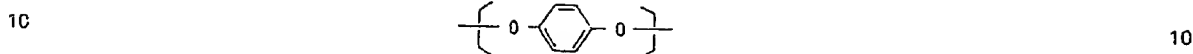
Desirable dicarboxyallyl unit II should be



desirable unit III should be



desirable dioxyallyl unit IV should be



Further, in the polymers adapted to form anisotropic melt phase of this invention, polymers in which part of their high molecular chain is composed of a segment of a polymer adapted to form anisotropic melt phase hereabove-described and the remaining part is composed of a segment of a thermoplastic resin not adapted to form anisotropic melt phase may be included. 15

The polymer composition of this invention adapted to form anisotropic melt phase and which is melt-processable may contain one or more of ① other polymers adapted to form anisotropic melt phase, ② thermoplastic resins not adapted to form anisotropic melt phase, ③ thermosetting resins, ④ low molecular organic compounds, ⑤ inorganic substances. The polymer segment adapted to form anisotropic fused phase and the remaining segment are allowed to be either thermodynamically compatible or not. 20

Included as the thermoplastic resins hereabove mentioned in ② are: e.g., polyethylene, polypropylene, polybutylene, polybutadiene, polyisoprene, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, polystyrene, acrylic resins, ABS resin, AS resin, BS resin, polyurethane, silicone resin, fluorine series resins, polyacetals, polycarbonates, polyethylene terephthalate, aromatic polyesters, polyamides, polyacrylonitrile, polyvinyl alcohol, polyvinyl ether, polyetherimide, polyamideimide, polyether etherimide, polyether ether ketones, polyether sulfones polyphenylene sulfide, polyphenylene oxide, etc. 25

Included as the thermosetting resins mentioned hereabove in ③ : e.g., phenol resins, epoxy resins, melamine resin, urea resins, unsaturated polyester resins, alkyd resins, etc. 30

Included as the low molecular organic compounds mentioned hereabove in ④ are; for example, substances which are to be added to general thermoplastic resins and thermosetting resins, which thus, include low molecular organic compounds used as plasticisers, light- and weather-proofing stabilizers like antioxidants or ultraviolet ray absorbers, etc., antistatic agents, fire retardants, coloring agents like dyes, pigments, etc., blowing agents, further, divinyl series compounds, bridging agents like peroxides or vulcanizing agents, etc., and lubricants for improving fluidity and mold releasing property, etc. 35

Further included as the inorganic substances mentioned hereabove in ⑤ are: e.g., materials to be added to general thermoplastic resins and thermosetting resins, which thus, include general inorganic fibers such as glass fibers, carbon fibers, metal fibers, ceramic fibers, boron fibers, asbestos, etc., powder materials such as calcium carbonate, highly dispersible silicic acid, alumina, aluminium hydroxide, talc powder, mica, glass flake, glass beads, quartz powder, silica sand, various metal powders, carbon black, barium sulfate, calcined plaster, etc., inorganic compounds such as silicon carbide, alumina, boron nitride, silicon nitride, etc., and whiskers and metal whiskers, etc. 40

In the polymer composition of this invention adapted to give anisotropic fused phase, its high molecular chains are highly oriented even in static state, when it is fused, and still higher orientation is achieved through flowing of the fused body, when being subjected to the fusion-forming. It is for this reason that still higher orientation is attained in the laminate film. 45

The thermoplastic polymer having film forming ability which is used for the laminate film of this invention needs to have a strength capable of bolstering its strength at least in the lateral axis direction relative to the direction of orientation of the thermotropic liquid crystal polymer as well as excellent film-forming ability by way of fusion-forming. Following polymers are illustrated: Polyethylene, polypropylene, polybutylene, polybutadiene, polyisoprene, polyvinyl acetate, polyvinyl chloride, polyvinylidene chloride, acrylic resins, ABS resins, AS resins, polyurethane, silicone resins, fluorine base resins, polycarbonates, polyethylene terephthalate, polybutylene terephthalate, aromatic polyesters, polyamides, polyacrylonitrils, polyvinyl alcohol, polyvinyl ether, polyether amide, polyamide imide, polyether etherimide, polyether etherketone, polyether sulfone, polysulfone, polyphenylene sulfide, ionomer, TPX and their copolymers. 50

Of these polymers, polyamide, polycarbonates, polyethylene terephthalate, polybutylene terephthalate, aromatic polyesters, polyether sulfone, polyether imide, polyether ether ketone, polyphenylene sulfide, etc., are desirable. 55

Usable as the method of forming the laminate film of this invention are a variety of methods hitherto used for film formation from thermoplastic resins; i.e., conventional methods comprising inflation process, T-die film-forming, calender process, flowing and drawing process and combinations of these drawing processes. When at least one type of layer of the multilayer laminate has been singly formed into a sheet or film beforehand, normal laminating devices and coating devices are usable. 60

Available as a preferable mode of exercising the method of this invention is a method in which a uniaxially oriented sheet adapted to form anisotropic melt phase is prepared and on this sheet, a thermoplastic 65

polymer having film forming ability is laminated by way of melt-processing as in the conventional laminate film forming method above-described.

While the individual sheets of polymer adapted to form anisotropic fused phase which compose such a laminate may be manufactured by arbitrary accustomed methods, forming the sheet by extruding through a slit die with appropriate dimensions under an adequate temperature and pressure, followed by fusion-drawing, is a preferable manufacturing method. The "sheet" used in this method may include a variety of all relatively thin, substantially flat structures which are sometimes called sheet, slab, film, etc., in said technical field. The thicknesses of individual sheets composing the laminate are not particularly restricted, but generally depend on the objects of use of the laminates; for example, the higher the strength required, the thicker sheets need to be used. The sheets manufactured in this way substantially give uniaxial or unidirectional orientation.

The existence of such uniaxial or unidirectional orientation may be determined by measurements of tensile characteristic (i.e., tensile strength of the sheet in both longitudinal (MD) and lateral (TD) directions in accordance with the U. S. Standard Test method ASTM D 882. When the ratio of tensile strength in the longitudinal direction of the sheet (direction of extrusion) to that in the lateral direction exceeds approx. 2.0 (preferably, within a range of approx. 2.0–100), there exists appropriate uniaxial orientation. Especially preferably, this ratio should be within approx. 10–50.

With regard to the conditions of temperature and pressure at which the liquid crystal polymer is extrudable for forming the sheet, this invention does not specify any particular limitations, but anyone in the trade is allowed readily to determine these conditions. In general, the extrusion of the thermotropic liquid crystal polymer may be performed at a temperature within a range (according to the fusion-temperature of polymer) of approx. 250–350°C and under a pressure within a range of approx. 7.0–350 kg/cm².

In order to ensure that the sheet as extruded give the desired uniaxial orientation, the extruded polymer melt should desirably be subjected to a drawing process. The drawdown ratio generally exceeds approx. 5.0. The drawn-out polymer is, then cooled or quenched by any appropriate means such as with use of cooling rolls, air blowing-in or water cooling, etc.

According to the method of this invention, on the high strength, highly oriented sheet of thermotropic liquid crystal polymer obtained in this way, a thermoplastic polymer having film forming ability may be laminated integrally therewith by way of melt-processing, using a laminating device such as that of T-die extrusion system or a coating device. This method is readily continuously exercised on industrial scale.

In this instance, the sheets to be laminated may be heated to temperatures higher than the fusion temperature of the polymer which composes the sheet without notably degrading the high degree of orientation the polymer shows. Since such a polymer maintains anisotropy even in its fused phase, use of adhesive, etc., may be spared when integrally joining sheets. However, as desired, the laminate may contain an adhesive phase as a third component.

As another preferable mode of exercising the method of this invention, the polymer adapted to form anisotropic fused phase and the thermoplastic polymer having film forming ability may be laminated by way of simultaneous melt-processing of both and the laminated sheet should desirably be subjected to a drawing process after melt-processing.

The mechanical properties of the laminate manufactured by the method of this invention sometimes may be further improved by subjecting it to a heat treatment after being formed.

[Embodiments]

This invention will become more apparent from descriptions taken in connection with embodiments thereof, but the modes of application of this invention is not restricted to these embodiments.

Examples 1 – 5

Pellets of thermotropic liquid crystal polymer obtained by polymerizing 75 mol % of p-hydroxybenzoic acid and 25 mol % of 6-hydroxy-2-naphthoic acid were dried at 140°C for 7 hours beforehand. Then a film 8.15 cm wide and 0.10 mm thick was obtained by extruding this polymer at a speed of 2.72 m/min, using a T-die type extruder. The fusion-drawdown ratio at this time was set at 14.3.

On the thermotropic liquid crystal polymer film thus obtained, polycarbonate (Lexan 8030 manufactured by Asahi Glass), nylon 12 (Diamide 4418 manufactured by Daicell Chemical Industry), polyethylene terephthalate (manufactured by Toray), polybutylene terephthalate (Duranex manufactured by Polyplastics) and polyacrylate (Durel manufactured by Occidental) were respectively laminated on a T-die extrusion type laminating device, yielding a laminate film 8.15 cm wide and 0.15 ± 0.05 mm thick.

With the laminate film thus obtained, its tensile strengths were measured in two directions – its main axial direction (MD) and in the direction (TD) at a right angle to the main axial direction. Results are shown in Table 1.

Example 6

A laminate film of thermotropic liquid crystal polymer obtained by polymerizing 75 mol % of p-hydroxybenzoic acid and 25 mol % of 6-hydroxy-2-naphthoic acid and polyethylene terephthalate was prepared by way of fusion-forming of both of them, using a multi-layer inflation film device and its tensile characteristics were measured. The results are shown in Table 2.

Example 7

A biaxially drawn laminate film was obtained by way of melt-processing of a thermotropic liquid crystal polymer obtained similarly as in Example 6 and polyethylene terephthalate, using a T-die type multi-layer extruding device and a biaxial drawing device.

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TABLE 1

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Tensile characteristics of laminate film

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*No.**Composition**Tensile
strengths*

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Comparison
Example 1 Thermotropic liquid crystal polymer
(T.LCP)

MD 477
TD 26.6

Example 1 T.LCP / Polycarbonate

MD 335
TD 64.7

Example 2 T.LCP / 12 Nylon

MD 391
TD 78.4

Example 3 T.LCP / Polyethylene terephthalate

MD 417
TD 96.0

Example 4 T.LCP / Polybutylene terephthalate

MD 402
TD 55.9

Example 5 T.LCP / Polyacrylate

MD 421
TD 63.7

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TABLE 2

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Film forming method and tensile strength

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*No.**Composition**Tensile
strengths*

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Example 6 2 Layer inflation film
T.LCP / Polyethylene terephthalate

MD 176
TD 118

Example 7 2 Layer extrusion biaxial drawing
T.LCP / Polyethylene terephthalate

MD 368
TD 174

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CLAIMS

1. A process for manufacturing a laminate sheet which comprises a film of a polymer adapted to form the anisotropic melt phase and a film of a thermoplastic polymer having the film-forming property by laminating at least one of both polymers.
2. A process as claimed in claim 1, in which the thermoplastic polymer is laminated on a uniaxially oriented film of the polymer adapted to form the anisotropic melt phase.
3. A process as claimed in claim 1, in which both polymers are moulded to film at the same time to laminate on each other.
4. A process as claimed in claim 3, which comprises a further step of stretching the obtained laminate sheet biaxially.